THE FORMIC ACID MONOMER: EXTENSION OF THE VIBRATIONAL DATABASE AND RIGOROUS ELECTRONIC AND NUCLEAR VIBRATIONAL STRUCTURE BENCHMARKS

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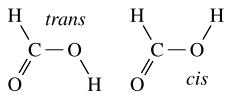

The vibrational spectroscopy of formic acid, F, has seen new and important experimental and theoretical impulses in the past six years.[a] In a combined experimental and theoretical approach, the vibrational database of F below 4000 cm^{-1} is reviewed and extended to 189 band centres [∼300% increase], including a plethora of highly-excited vibrational states, both torsional conformers, and several isotopologues [^{1}H, ^{2}H, ^{12}C, ^{13}C, and ^{16}O].[b] Essentially, the vibrational characterisation of its skeletal modes below 3500 cm^{-1} can be regarded as complete which is also an important stepping stone in understanding the complex vibrational dynamics of its cyclic dimer.[c] A new key insight is that the impact of the OH bend-torsion resonance [ν_5 and $2\nu_9$] on the entire vibrational dynamics of *trans*-HCOOH is more far-reaching than previously believed. Beyond 3500 cm^{-1}, which is also near the expected *trans*→*cis* isomerisation threshold, this resonance polyad is indicated to play an important role in the perturbations of the OH stretching fundamental [ν_1]. In this contribution, new spectroscopic developments are summarised and promising future research directions for F are discussed. In particular, its importance and suitability for the purpose of benchmarking electronic and nuclear vibrational methodologies are highlighted.

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[a] (exp) K. Hull, T. Wells, B. E. Billinghurst, H. Bunn, P. L. Raston, *AIP Adv.* **2019**, *9*, 015021; K. A. E. Meyer, M. A. Suhm, *Chem. Sci.* **2019**, *10*, 6285; A. Nejad, M. A. Suhm, K. A. E. Meyer, *Phys. Chem. Chem. Phys.* **2020**, *22*, 25492. (theo) D. P. Tew, W. Mizukami, *J. Phys. Chem. A* **2016**, *120*, 9815; F. Richter, P. Carbonnière, *J. Chem. Phys.* **2018**, *148*, 064303; A. Aerts, P. Carbonnière, F. Richter, A. Brown, *J. Chem. Phys.* **2020**, *152*, 024305; A. Nejad, E. L. Sibert III, *J. Chem. Phys.* **2021**, *154*, 064301.

[b] A. Nejad, PhD thesis, submitted (2022).

[c] A. Nejad, K. A. E. Meyer, F. Kollipost, Z. Xue, M. A. Suhm , *J. Chem. Phys.* **2021**, *155*, 224301